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COMPUTATIONAL INVESTIGATIONS OF SYMMETRY AND COUPLED SUBSTITUTIONS IN NATROLITE GROUP MINERALS

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ABSTRACT

Empirical interatomic potentials and energy minimisation techniques were used to test atomic configurations of two minerals of the NAT zeolite topology, natrolite and gonnardite. The natrolite structure (Artioli et al., 1984) was found not to be stable in the empirical *Fdd*2 space group. With symmetry constraints released during minimisation, the structure relaxed either with a slight triclinic distortion or to an unphysical configuration, though intermediate steps during minimisation showed first monoclinic and later triclinic symmetry. In the gonnardite structure (Artioli and Torres Salvador, 1991), simulations with full cation disorder but only some of the extraframework water molecules included showed a positive correlation between the cell parameters and Ca content. Since the averaging of potentials does not properly represent disorder in extraframework and coupled sites, we instead built a model structure with full order in extraframework cation sites and the proper number of water molecules. Energetically favourable locations for H_2O molecules relative to Ca atoms were found only in the latter model.

Key words: natrolite, gonnardite, energy minimisation, disorder

INTRODUCTION

A few years ago an unusual fibrous zeolite mineral was found in two samples from two localities in the Balaton Highlands basalt occurrences. The most apparent unusual quality is an evident oblique extinction on the prism faces, while the morphology is not distinguishable from that of natrolite. Detailed optical studies, using a spindle stage, revealed low refractive indices and a $2V$ similar to those of natrolite, but an orientation of the principal axes of refraction suggesting monoclinic symmetry, unlike orthorhombic natrolite (Váczi, 2000). Nothing similar had been described before in the literature.

Another existing issue in the investigation of the group of the so-called fibrous zeolites is the question whether any distinction between gonnardite and tetranatrolite is valid or not. Tetranatrolite has been found to have the same crystal structure (Evans et al., 2000) as gonnardite (Mazzi et al., 1986). Some authors insist on a definite distinction between the two ranges of composition (*e.g.* Evans et al., 2000), however, according to the IMA CNMMN nomenclature guidelines, the two phases should not be defined as separate species because the dominant cation is Na in both cases.

In this paper we present preliminary calculations aimed at investigating the stability and structure of natrolite and gonnardite. We describe the initial attempts in the search for the energetically most favourable atomic configurations of these minerals, concentrating on either their possible symmetry or the nature and location of secondary cations and H_2O. Our ultimate aim is to test whether a Na-rich monoclinic member of the natrolite group (Váczi, 2003) is energetically possible and to find new insights into the gonnardite/tetranatrolite debate.

THE NAT TOPOLOGY

Both structures considered in this paper share the NAT (named after natrolite) framework topology, differentiated by the presence or the lack of Si-Al order in tetrahedral positions. The NAT topology can be best described using its secondary building units (SBU's). It is made up of the 4-1 SBU, which consists of a ring of 4 tetrahedra, with two vertices of opposite tetrahedra linked above or below the 4-fold ring with a fifth tetrahedron (Fig. 1). These SBU's line up to form long chains along the crystallographic *c* direction.

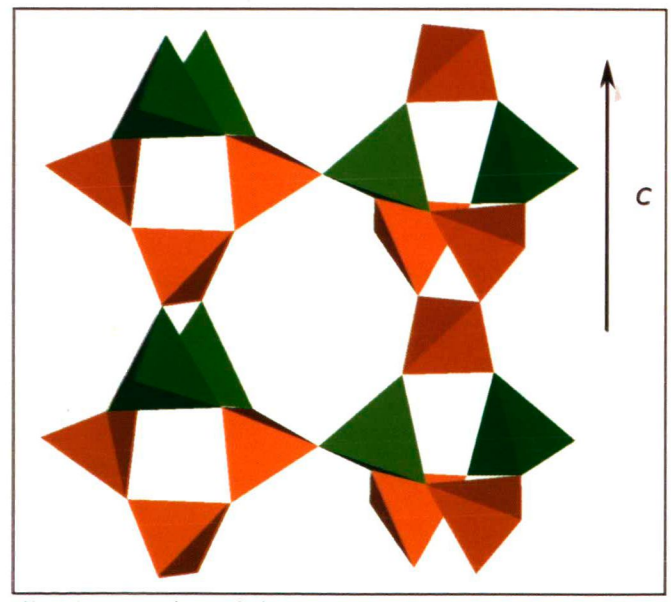

Fig. 1. A section of the natrolite framework, showing the linking of SBU's in the NAT topology. Orange tetrahedra: SiO_4, green tetrahedra: AlO_4.

The chains are connected laterally with a ¼ c shift such that in the topological arrangement there is a fourfold screw axis in the channel between four chains (space group $I4_1/amd$).

Structures and Simulations

Lattice energy minimisation was performed with the GULP code (Gale, 1997). This program searches for a local minimum in lattice energy *i.e.* a configuration in which the net force acting on every atom is zero. This optimisation may encompass all atomic coordinates and the unit cell parameters or may be restricted to a subset of these variables. Each simulation requires an initial structure, which may be taken directly from the literature or modified to form a hypothetical structure, and a set of interatomic potentials describing the interaction between pairs and triplets of atoms (Table 1). The potentials used were those employed by Higgins et al. (2001) in their study of water and cation exchange in zeolite A.

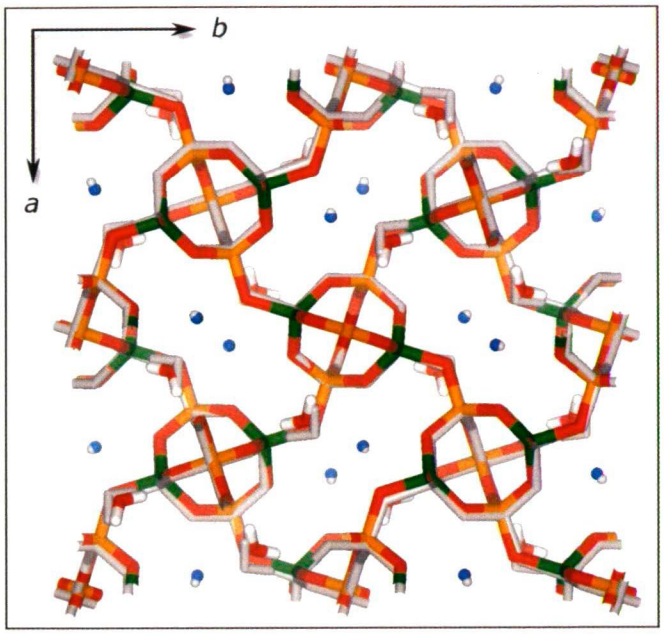

Fig. 2. The original (grey) and relaxed (coloured) configuration of the natrolite structure, matched at the centre of the unit cell. Orange: Si, green: Al, red: O, blue: Na, white: H.

Table 1. Interatomic potential parameters (from Higgins et al., 2001). O1 is oxygen in the framework, O2 is oxygen in H_2O.

Species	Charge (e)	Species	Charge (e)	Core–shell interaction (eV Å^{-2})
Si	+4.0	O1 (core)	+0.86902	74.92
Al	+3.0	O1 (shell)	–2.86902	
Na	+1.0	O2 (core)	+1.25	209.449602
Ca	+2.0	O2 (shell)	–2.05	
		H	+0.4	

Buckingham				
	A (eV)	ρ (Å)	C (eV Å^6)	cut-off (Å)
Si–O1	1283.907	0.32052	10.66158	18.5
Si–O2	562.032	0.32052	10.66158	18.5
Al–O1	1460.30	0.29912	0.0	18.5
Al–O2	584.1107	0.29912	0.0	18.5
Ca–O1	1090.40	0.3437	0.0	18.5
Ca–O2	436.16	0.3437	0.0	18.5
Na–O1	5836.814	0.2387	0.0	18.5
Na–O2	4088.384	0.2387	0.0	18.5
O1–O1	22764.00	0.1490	27.88	18.5
O1–O2	22764.00	0.1490	28.92	18.5

Lennard–Jones			
	A (eV Å^{12})	B (eV Å^6)	cut-off (Å)
O2–O2	39344.98	42.15	20.0

Morse				
	D (eV)	a (Å^{-1})	r_0 (Å)	cut-off (Å)
H–O2	6.203713	2.22003	0.92376	2.0

Three-body			
	k (eV rad^{-2})	θ_0 (°)	cut-off (Å)
O1–Si–O1	2.09724	109.47*	3.0
O1–Al–O1	2.09724	109.47	3.0
H–O2–H	4.19980	108.69319*	2.0

Coulombic subtraction		cut-off (Å)
H–O2 (core)	0.5	1.2
H–O2 (shell)	0.5	1.2
H–H	0.5	2.4

*We suspect that these two parameters were erroneously transposed in Higgins et al. (2001), but we have used the potentials as published there. Test calculations with values of these parameters as in this Table did not find substantially different results; further investigation is ongoing.

Ordered Framework with Na (Natrolite)

The first structure investigated in detail was natrolite (Artioli et al., 1984). Natrolite is orthorhombic, with space group $Fdd2$. Its ideal formula is $Na_2Al_2Si_3O_{10}{\cdot}2H_2O$ (Z = 8). The symmetry is lowered from the topological $I4_1/amd$ because Si and Al are fully (or strongly) ordered over 3 distinct sites and the chains rotate along c. The channels contain Na and H_2O.

The optimisation was performed using the entire unit cell with the symmetry constraints lifted ($P1$). A stable structure was found after 12 cycles of optimisation. During relaxation the cell parameters contracted, the a axis more than b. Thus the b–a value (0.632 Å), indicative of the degree of disorder in natrolite (Alberti and Vezzalini, 1981), is significantly more than the empirical 0.35 Å maximum for fully ordered structures. Relaxed cell parameters are slightly shorter than the experimental ones (by 0.631 Å for a, 0.340 Å for b, 0.003 Å for c). The largest (though still small) difference between initial and relaxed coordinates is found in H_2O molecules (Fig. 2). The structure stabilised with a slight monoclinic distortion, β = 90.052°. The symmetry is found to be $P1$ with a tolerance of 0.001 Å in atomic coordinates. (The space group is measured to be Cc with tolerances 0.002–0.011 Å and the original $Fdd2$ with a tolerance of 0.012 Å and more.)

Another simulation used only the asymmetric unit as input to optimisation. In this case the results are different: the structure collapses after more than 100 optimisation cycles. The unit cell distorts as optimisation proceeds: the triclinic distortion is minimal in the first 100 cycles and is greatest for the β angle, but then increases dramatically and in just a few steps leads to the collapse of the structure (i.e., unfeasible atomic distances and lattice energy). The distortion is shown in Fig. 3 by the outlines of the generated unit cells after 0, 120 and 123 cycles, the values of unit cell angles are listed in Table 2.

Disordered Framework with Ca Substitution (Gonnardite and Tetranatrolite)

Gonnardite and tetranatrolite – according to the present IMA CNMMN guidelines, the name tetranatrolite is discredited (Artioli and Galli, 1999). The original description of the phase by Chen and Chao (1980) states that tetranatrolite is a dehydration phase of paranatrolite, in agreement with the opinion of Ross et al. (1992) and Evans et al. (2000). Paranatrolite is a superhydrated phase, which dehydrates irreversibly in atmospheric conditions. Tetranatrolite and paranatrolite usually form crusts on natrolite crystals, with a sharp interface between natrolite and the crust. Gonnardite, on the other hand, occurs as radial fibrous crystal aggregates, not necessarily associated with natrolite (Ross et al., 1992) – share the same NAT topology of the tetrahedral framework as natrolite (Mazzi et al., 1986; Evans et al., 2000). There is a complete (Si,Al) disorder over tetrahedral sites and complete (Na,Ca) disorder over the extraframework (Na,Ca) sites, hence the symmetry is tetragonal $I\bar{4}2d$. The distinction, if any, can be made on the basis of the Si/Al ratio (Si/Al < 1.5 for gonnardite and Si/Al ≥ 1.5 for tetranatrolite; Artioli and Galli, 1999) or an apparent gap in chemistry (gonnardite having compositions along the natrolite–thomsonite join, represented by the formula $\square_x Na_{16-3x}Ca_{2x}Al_{16+x}Si_{24-x}O_{80}\cdot nH_2O$, and tetranatrolite along the natrolite–"ideal tetranatrolite" join, with a formula $Na_{16-x}Ca_xAl_{16+x}Si_{24-x}O_{80}\cdot 16H_2O$; for more details see Ross et al., 1992).

An initial tetragonal structure was taken from Artioli & Torres Salvador (1991) and H positions were added by analogy with natrolite.

We first investigated the effect of Ca on cell dimensions. Assuming no extraframework cation vacancy, structures with compositions $Na_{8-x}Ca_xAl_{8+x}Si_{12-x}O_{40}\cdot 8H_2O$, with x = 0–2, were generated in x = 0.5 increments (Z = 1). Si-Al and Na-Ca disorder was full over T and (Na,Ca) sites, respectively. $W2$, for reasons described below, was omitted from the structure. ($W2$ enters the structure to increase the coordination of Ca from six- to sevenfold). The results show, as expected, that increasing Ca content causes a slight increase in cell dimensions (Table 3).

The presence of $W2$ in the model was found to be problematic for simulation. Normally, shared or partial occupancy would be used over the entire lattice, all equivalent positions having the same occupancy. However, in the case of locally coupled substitution such as (Ca + H_2O + Al) ↔ (Na + Si) it is inappropriate to introduce a fraction of Ca to all (Na,Ca) sites and to add a fractional H_2O molecule to the coordination polyhedron of each of them since Ca and $W2$ are assumed to be always present together. Such a model, though

Table 3. Change in relaxed cell parameters of the gonnardite structure as a function of Ca content (for O_{40}).

	a (Å)	c (Å)	V (Å^3)
Experiment*	13.125	6.622	1140.743
Ca = 0	12.581	6.495	1028.039
Ca = 0.5	12.592	6.530	1035.387
Ca = 1	12.599	6.562	1041.618
Ca = 1.5	12.601	6.595	1047.188
Ca = 2	12.601	6.625	1051.952

*Artioli & Torres Salvador (1991), sample 1. The authors used Ca ≈ 1.7 for the refinement.

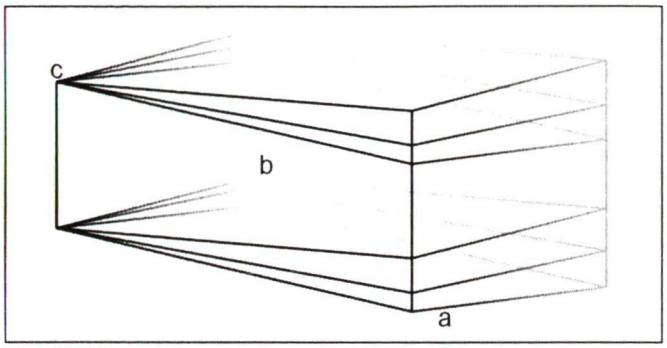

Fig. 3. The outlines of the unit cell show the distortion of the natrolite structure during minimisation at steps 0, 120 and 123.

Table 2. Distortion of the unit cell of natrolite during symmetry-off simulation.

Calculation cycles	Unit cell dimensions (Å)			Angles (°)		
	a	b	c	α	β	γ
0 (experiment)	18.27	18.61	6.59	90.0	90.0	90.0
20	17.66	18.27	6.59	90.0	90.3	90.0
80	17.65	18.28	6.59	90.0	90.4	90.0
100	17.64	18.30	6.58	90.0	90.5	90.0
120	17.55	18.46	6.48	91.4	95.1	89.1

consistent with the data set of structure refinements, is an inaccurate description of these structures.

To avoid the problem of fractional H_2O molecules, a structure without long-range tetragonal symmetry was built by taking just one possible Na-Ca arrangement of a single unit cell and generating a set of atomic positions with space group $P1$. This approach gives total independent control over each atomic position in the entire unit cell. By taking a snapshot of the system, it gives the advantage of employing full occupancy in all extraframework sites, though at the expense of having the same periodic arrangement of Ca substitution over the entire lattice.

Representing disorder by average occupancy was maintained for the framework cation distribution. The full occupancy approach for T sites was rejected for the reason that the maximum number of possible distributions of Al and Si atoms over 20 T sites per unit cell is high (125970), though the number of unique configurations worth considering would be fewer e.g. by eliminating symmetry-related ones and applying Loewenstein's rule (Ruiz-Salvador et al., 1998).

Due to the space group symmetry all (Na,Ca) sites are equivalent in the gonnardite/tetranatrolite structure, i.e. in the case of one Ca for Na substitution per unit cell it should not matter which site is chosen. Any (Na,Ca) site is coordinated by four tetrahedral oxygens and two (for Na) or three (for Ca) H_2O molecules. The structure refinements of Artioli and Torres Salvador (1991) and Evans et al. (2000) show that at ambient temperature O($W2$) may be split between two close-lying sites, 0.8–1.5 Å apart, related by a twofold symmetry axis. On the other hand, Artioli and Galli (1999) did not find any evidence for split extraframework sites in gonnardite.

In the structural description the split site with a fractional occupation is a time-averaged phenomenon; i.e. the two halves are not occupied at the same time. Therefore, in the case of 1 Ca + H_2O substitution per unit cell, we checked two options by simulation: (1) single H_2O in only one of the split $W2$ sites or (2) at the midpoint of the two, in both cases with full occupancy.

It was found that a split site position is unfavourable for the H_2O molecule: it moves away from its initial location towards the framework. By "probing" different locations for *W*2 by locking everything but the single *W*2 molecule in place, the average of the split site (special position, located on a diad) was the only position where an energy minimum was found. This result for the relaxed position of *W*2 is consistent with the structural data of Artioli and Galli (1999). Therefore, in the rest of the simulations initial coordinates of *W*2 were set accordingly.

The tetrahedral neighbourhood of secondary cations is another issue requiring careful control of coupled substitution. The closest two *T* sites are at a distance of approximately 3.15 Å from the (Na,Ca) site, and, according to Pauling's electrostatic valence rule and the principle of local electroneutrality (solids must be electrostatically neutral not only on the whole but on a small scale as well; Armbruster and Gunter, 2001), one would expect Al/Si substitution accompanying Ca to take place in one of these closest spaced sites. These two closest sites are at equal distances, but there is only one surplus charge to locate for each Ca-Na substitution. It was chosen instead that generally all *T* sites were given 0.6 Si and 0.4 Al occupancy but these two closest have the surplus charge shared equally (0.1 Si, 0.9 Al). A single *T* site cannot formally be given all the surplus charge and it was chosen not to "overcharge" one site because the ensuing asymmetry would cause an undesired distortion of the Ca coordination polyhedron, possibly displacing the Ca ion itself from a special position.

The next step was to introduce a second Ca + *W*2 pair into the unit cell. Several different configurations were examined: 2 Ca in the same channel, 1-1 in adjacent channels or diagonally across the unit cell, the latter with Ca's at either of the two possible sites. Optimisation was performed only on channel contents. It was possible to relax most of the structures (Table 4), although some calculations could only be optimised to unstable configurations. The most acceptable configuration, including the orientation of water molecules, was the one with a pair of Ca atoms in diagonal channels and at the same *c* height (Fig. 4).

Discussion

The most unexpected of our preliminary results is the distortion of the natrolite structure, the reason for which is unknown: a stable structure should not lower its symmetry during minimisation, even without symmetry constraints. Although we have not yet unambiguously determined a robustly stable configuration, the distortion of the natrolite structure, observed in all cases, may indicate that the orthorhombic experimental structure is not stable at zero temperature (data for the structure refinement were collected at 20 K; Artioli et al., 1984). In a previous case where a similar breaking of symmetry was found experimentally in silicalite, the resulting stable distorted structure was confirmed by simulation (Bell et al., 1990).

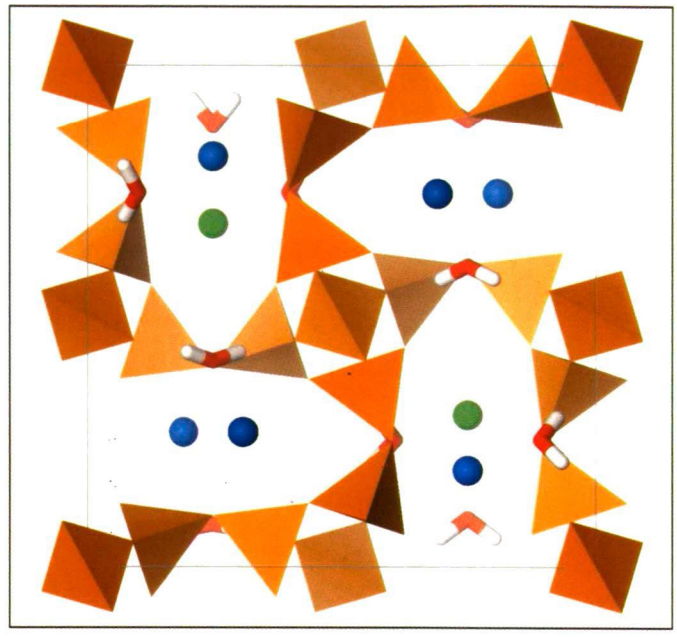

Fig. 4. The most favourable relaxed positions of extraframework contents of the gonnardite structure for 2 Ca per unit cell. Tetrahedra: $(Si,Al)O_4$, blue balls: Na, green balls: Ca, red-white sticks: H_2O.

Table 4. Summary of selected simulated structures and configurations.

Structure	Asymm. unit/ Full cell	Symmetry	Disorder	Ca+*W*2 (for O_{40})	Optimised components FW	eFW+*W*1	*W*2	Relaxed
natrolite								
natrolite	A	*P*1	no	0	+	+		no
natrolite	F	*P*1	no	0	+	+		yes
gonnardite								
gonnardite	A	$I\bar{4}2d$	FW + eFW	0	+	+		yes
gonnardite	A	$I\bar{4}2d$	FW + eFW	1	+	+		yes
gonnardite	A	$I\bar{4}2d$	FW + eFW	2	+	+		yes
gonnardite	F	*P*1	FW	1	+	+	+	no
gonnardite	F	*P*1	FW	1	–	–	+†	no
gonnardite	F	*P*1	FW	1	–	–	+‡	yes
gonnardite	F	*P*1	FW	2	–	+	+	yes

Natrolite input structure: Artioli et al. (1984); gonnardite: samples 1 & 3 from Artioli & Torres Salvador (1991), with H atoms added. Symmetry shows what space group was enforced during optimisation; *P*1 means no symmetry constraints. Asymm. unit/full cell means whether only coordinates of the asymmetric unit and symmetry were given at input to generate the cell or the full coordinate set was given at input. Ca content is in atoms p.f.u. for gonnardite, $Z = 1$. FW includes *T* sites and framework oxygens, eFW + *W*1 means all channel contents except *W*2. Empty cells mean not applicable or not present.
† *W*2 in split site; ‡ *W*2 in special position – see text for details.

The difference in the results between using the asymmetric unit and the full cell at input in the case of natrolite also requires special attention. The full cell was generated from the set of atomic coordinates for the asymmetric unit using the GULP program. This sensitivity to the method of setting up the structure in the case of natrolite requires further investigation. A more thorough treatment of the natrolite structure may be necessary (e.g. molecular dynamics or Monte Carlo simulations).

We employed general interatomic potentials for the framework and the framework–secondary cation interactions, while the cation–O(*W*2) potentials were fitted to a zeolitic system (zeolite A; Higgins et al., 2001). An explanation for the observed distortion could be that some of the interatomic potentials are not fully adequate to describe forces acting in the natrolite structure. It can be seen on Fig. 2 that, apart from the difference in the unit cell size, the water molecules show the largest (though still not great) deviation from their experimentally determined positions and shape. The shortening of cell parameters compared to experimental values may indicate that the channel contents are artificially small with these potentials.

In the case of gonnardite, initial investigations of possible positions for H_2O and Si/Al substitution coupled to Ca/Na substitution have found some stable configurations. In particular, a split site model for H_2O was not supported and instead a single averaged position was found to be stable. Further calculations would be needed with larger unit cells, applying a defect model and/or molecular dynamics (in order to study finite temperature effects and disorder) in order to confirm the structures suggested here.

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REFERENCES

ALBERTI, A., VEZZALINI, G. (1981): A partially disordered natrolite: relationships between cell parameters and Si-Al distribution. Acta Crystallographica B, **37**, 781–788.

ARMBRUSTER, T., GUNTER, M. E. (2001): Crystal structures of natural zeolites. In Bish, D.L., Ming, D.W. (eds.): Natural zeolites: Occurrence, properties, applications. Reviews in Mineralogy and Geochemistry, **45**, 1–67.

ARTIOLI, G., GALLI, E. (1999): Gonnardite: Re-examination of holotype material and discreditation of tetranatrolite. American Mineralogist, **84**, 1445–1450.

ARTIOLI, G., TORRES SALVADOR, M. R. (1991): Characterization of the natural zeolite gonnardite. Structure analysis of natural and cation exchanged species by the Rietveld method. Materials Science Forum, **79–82**, 845–850.

ARTIOLI, G., SMITH, J. V., KVICK, Å. (1984): Neutron diffraction study of natrolite, $Na_2Al_2Si_3O_{10}{\times}2H_2O$, at 20 K. Acta Crystallographica C, **40**, 1658–1662.

BELL, R. G., JACKSON, R. A., CATLOW, R. A. C. (1990): Computer simulation of the monoclinic distortion in silicalite. Journal of the Chemical Society, Chemical Communications 1990, 782–783.

CHEN, T. T., CHAO, G. Y. (1980): Tetranatrolite from Mont St-Hilaire, Québec. Canadian Mineralogist, **18**, 77–84.

EVANS, H. T., KONNERT, J. A., ROSS, M. (2000): The crystal structure of tetranatrolite from Mont Saint-Hilaire, Québec, and its chemical and structural relationship to paranatrolite and gonnardite. American Mineralogist, **85**, 1808–1815.

GALE, J. D. (1997): GULP: A computer program for the symmetry-adapted simulation of solids. Journal of the Chemical Society – Faraday Transactions, **93**, 629–637.

HIGGINS, F. M., DE LEEUW, N. H., PARKER, S. C. (2002): Modelling the effect of water on cation exchange in zeolite A. Journal of Materials Chemistry, **12**, 124–131.

MAZZI, F., LARSEN, A. O., GOTTARDI, G., GALLI, E. (1986): Gonnardite has the tetrahedral framework of natrolite: experimental proof with a sample from Norway. Neues Jahrbuch für Mineralogie, Monatshefte 1986, 219–228.

ROSS, M., FLOHR, M. J. K., ROSS, D. R. (1992): Crystalline solution series and order-disorder within the natrolite mineral group. American Mineralogist, **77**, 685–703.

RUIZ-SALVADOR, A. R., LEWIS, D. W., RUBAYO-SONEIRA, J., RODRÍGUEZ-FUENTES, G., SIERRA, L. R., CATLOW, R. A. (1998): Aluminum distribution in low Si/Al zeolites: Dehydrated Na-clinoptilolite. Journal of Physical Chemistry B, **102**, 8417–8425.

VÁCZI, T. (2000): Optical properties of fibrous zeolites of the Bakony–Balaton Highlands, Hungary. Acta Mineralogica-Petrographica, **41**, Supplementum, 116.

VÁCZI, T. (2003): Mineralogical–crystal chemical investigations on fibrous zeolites from Hungary. M.Sc. thesis. Budapest: Department of Mineralogy, Eötvös L. University. 68 p. (in Hungarian with English abstract)